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(54) Preparing Olefin Polymerisation Catalysts

(57) A process for the preparation of an olefin polymerization catalyst comprising reducing TiCl_4 with an organo aluminium compound in the presence of a dialkyl ether, characterized in that TiCl_4 is reduced with trihydrocarbly aluminium

compound in a molar ratio of Ti:Al of at least 2.7:1 in the presence of di-isoamylether and a hydrocarbon solvent by gradually combining the reactants at a temperature of from 65 to 90°C during a period of from 1.2 to 5 hours to produce a precipitate of brown TiCl_3 , whereupon this precipitate is activated by heating at a temperature of from 80 to 110°C during a period of at least 30 minutes.

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employ higher temperatures. Another preferred way of producing attractive catalysts is by premixing both the trihydrocarbonyl aluminium compound and TiCl_4 with diisoamylether before one reactant is added to the other, when doing so it is recommended to employ Ti: ether molar ratios in between 0.8:1 and 3:1, preferably of from 1.0:1 to 2.4:1 and Al:ether molar ratios in between 2:1 and 0.3:1, preferably of from 1.4:1 to 0.6:1.

At the end of the gradual combining of the reactants participating in the reduction reaction, reduction may not be entirely complete. In such event the reaction mixture is kept at the same or slightly higher temperature, under stirring, for a period of up to 2 hours, dependent upon the addition period and temperature employed for combining the reactants. The reduced reaction product is obtained in the form of a suspension of fine solid particles in a liquid medium. The solid particles predominantly have the brown colour of beta- TiCl_3 .

This brown TiCl_3 is then activated by heating at a temperature of from 80 to 110°C for at least 30 minutes, and more preferably at a temperature of from 85 to 95°C for a period of from 0.75 to 2.5 hours. It is recommended to observe the growth of the size of the TiCl_3 particles during the reduction reaction and not to start with the activation before there is no further growth of particle size. Any agglomeration of particles during activation should be avoided and this can normally be achieved by stirring under controlled conditions.

The activated catalyst finally obtained is characterized by having a colour which is neither the typical brown colour of the beta-modification of TiCl_3 nor the typical violet colour of the gamma— or delta-modification. Instead the colour may at best be referred to as "brown/violet". To remove any remaining unreacted material from the catalyst, the latter may be washed with an aliphatic or aromatic hydrocarbon solvent.

In the polymerization of olefins the catalyst is used together with conventional organo-aluminium compounds often referred to as "activator" or "cocatalyst". Typical representatives of such compounds are aluminium diethyl chloride, aluminium diisopropyl chloride, aluminium ethyl sesquihalogenide and the like. In general the activator can be any compound of the general formula $\text{AlR}_n\text{X}_{3-n}$, where R is alkyl with 2—8 carbon atoms and n is any number of from 1 to 3, preferably 2, and X is halogen, preferably chlorine.

Before polymerization is started one or both of the components forming the catalytic system or the catalyst system per se can be reacted with a non-enolizable carbonyl compound to increase the stereospecific performance of the system. Suitable compounds are esters, ketones, aldehydes and organic carbonates in which the alpha-carbon atom (with respect to the carbonyl group) is a tertiary carbon atom or a secondary

carbon atom which carries a hydrogen atom to which access is difficult because of steric hindrance, or a carbon atom forming part of an aromatic ring structure. Suitable carbonyl compounds are di-t-butyl ketone, di-isopropyl ketone, isopropyl-t-amyl ketone, diethyl carbonate, diethyl terephthalate, benzophenone, diphenyl carbonate, p-methoxyethyl benzoate, ethyl acrylate, ethyl methacrylate, methyl methacrylate, ethyl benzoate and p-ethoxymethyl benzoate. Other compounds which may be used for the same purpose are strong Lewis bases, such as trialkyl amines, trialkyl phosphines or trialkyl borates. It is also possible, albeit less preferred, to employ any of such compounds improving the stereospecificity of the catalytic system by incorporating them simply in the polymerization mixture.

Polymerization of olefins with the catalysts of this invention can be effected by any conventional method, for example by the gas phase or liquid bulk method or by slurry polymerization in the presence of an inert hydrocarbon solvent. In order to terminate the polymerization, the catalyst can be deactivated by any known means, e.g., by addition of an aliphatic alcohol, such as ethanol or butanol, ketones, such as methyl ethyl ketone or methyl isobutyl ketone, acetone, ethers, e.g., tetrahydrofuran, or similar compounds.

Hydrogen may be employed during polymerization to achieve molecular weight control. When doing so, it is recommended to employ H_2 —concentrations of from 0.5—5% vol., preferably 1—3% vol.

Example 1

a) Preparation of activated TiCl_3

A solution comprising 33.3 mmol. aluminium triethyl, 33.3 mmol. di-isoamyl ether and 160 ml toluene was added dropwise over a period of 3 hours at 70°C to a solution comprising 200 mmol. TiCl_4 , 110 mmol. di-isoamyl ether and 100 ml toluene. Thereafter stirring was continued for 70 minutes at 70°C and 50 minutes at 75°C.

The resulting suspension of brown TiCl_3 was heated at 90°C during 60 minutes to produce activated TiCl_3 having a brown/purple colour. Hydrocarbon solvent was removed from the suspension by decantation and the catalyst was washed five times with iso-octane. The TiCl_3 so obtained had a particle size of 10—20 μm , all particles were of a regular, round shape. The particle size distribution was very even.

b) Polymerization

1.7 mmol. activated TiCl_3 was introduced into a 3 l reaction vessel comprising 9 mmol. diethyl aluminium chloride and 1.5 l of iso-octane. The reactor was pressurized with propylene to 255 kPa and polymerization was effected at 70°C during 4 hours in the presence of 1% vol. of hydrogen. The polymerization was stopped by deactivating the catalyst with butanol. The polymer was washed with 1% aq. HCl and three times with water. After steam distillation the

polymer was filtered off and dried.

In this standard polymerization run the activated TiCl_3 catalyst showed an activity, expressed as gram polymer per gram catalyst per hour per 98 kPa, of 173. The stereo-specificity of the catalyst, expressed as percentage of polymeric material that remained soluble when cooling a solution of polymer in xylene from its boiling point to room temperature, was 8.1. The same polymerization run is used as a standard test in Examples 2 to 9, and comparative Examples A to F.

Example 2

Example 1 was repeated, now using 40 ml of toluene instead of 160 ml in the aluminium triethyl solution and adding the reactants during a period of 3.5 hours instead of 3 hours. When the addition of the reactants was completed, stirring was continued for 2 hours at 70°C. All other reaction conditions remained unchanged.

The polymerization test now showed an activity of 193 g/g TiCl_3 /h/98 kPa, the stereospecificity was 6.1%. The purple/brown catalyst comprised regular, round particles with a uniform size of 12 to 13 μm .

Example 3

Example 1 was repeated now employing a TiCl_4 -solution comprising 134 mmol. di-isoamyl ether, an activation period of 35 minutes, and an addition period of 3.5 hours. All other conditions remained unchanged. A catalyst was obtained having a similar colour and morphology as indicated in Example 1.

The polymerization activity was 177 g/g TiCl_3 /h/98 kPa, the stereospecificity was 10.0%.

Example 4

Example 3 was repeated using an activation period of 1 hour but otherwise the same conditions. Again, the catalyst had a similar colour and morphology. The polymerization test showed an activity of 152 g/g TiCl_3 /h/98 kPa, the stereospecificity was 9.7%.

Example 5

Example 4 was repeated under the same conditions except that after the addition stirring was continued for 2 hours at 70°C. The catalyst had a purple/brown colour and an excellent morphology comprising regular round particles with a size of 10–20 μm and an even particle size distribution. The polymerization activity was 148 g/g TiCl_3 /h/98 kPa, the stereospecificity was 8.6%.

Example 6

Example 5 was repeated employing a TiCl_4 -solution comprising 170 mmol. di-isoamyl ether and an AlEt_3 -solution comprising 43.3 mmol. AlEt_3 instead of 33.3 mmol., but otherwise the same conditions. The catalyst had a similar colour and morphology as indicated in Example 5. The

polymerization activity was 183 g/g TiCl_3 /h/98 kPa, the stereospecificity was 8.8%.

Example 7

Example 5 was repeated now employing an addition period of 2 hours and continuing stirring at a gradually increasing temperature of 65 to 90°C during 5 hours. All other conditions remained unchanged. The colour and morphology of the catalyst were identical to those indicated in Example 5. The polymerization activity was 176 g/g TiCl_3 /h/98 kPa, the stereospecificity was 9.8%.

Example 8

Example 7 was repeated while adding a solution comprising 770 mmol. aluminium triethyl, 1000 mmol. di-isoamyl ether and 3700 ml toluene to a solution comprising 4600 mmol. TiCl_4 , 3900 mmol. di-isoamyl ether and 2300 ml toluene. The remaining conditions were unchanged. The polymerization activity of the purple/brown catalyst was 167 g/g TiCl_3 /h/98 kPa, the stereospecificity was 10.2%, the morphology of the catalyst was identical to that described in Example 5.

Comparative Examples A—F

A. Example 5 was repeated whilst omitting the activation treatment at 90°C. The catalyst so obtained had a good morphology and a purple/brown colour; however, the polymerization activity was 134 g/g TiCl_3 /h/98 kPa and the stereospecificity was 12.4%.

B. Example 5 was repeated using di-butyl ether instead of di-isoamyl ether but leaving the molar amounts of ether and all other conditions unchanged. The polymerization activity was 116 g/g TiCl_3 /h/98 kPa, the stereospecificity was 1.8%. The colour was brown/purple but the morphology was irregular showing an uneven particle size distribution, the size of the particles ranged from 20 to 50 μm and a substantial portion of the particles had an irregular shape.

C. Example 5 was repeated employing an addition period of 30 minutes and an activation period of 25 minutes leaving all other conditions unchanged. The polymerization activity of catalyst so produced was 112 g/g TiCl_3 /h/98 kPa and the stereospecificity was 9.1%. Catalyst morphology showed irregular particles of from 30 to 60 μm and uneven particle size distribution.

D. Example 5 was repeated now using diethyl aluminium chloride (50 mmol.) instead of aluminium triethyl. Also the amount of di-isoamyl ether in the TiCl_4 -solution was lowered to 110 mmol., all other conditions remained the same. The activity of the catalyst was 83 g/g TiCl_3 /h/98 kPa. The stereospecificity was 12.0%.

E. Example 5 was repeated whilst adding the reactants participating in the reduction reaction dropwise at 35°C during a period of 3.5 hours. Thereafter the suspension was stirred for one hour at 35°C and heated at 65°C for two hours. All other conditions remained unchanged. The

* *bedenket : Agglomerate*

catalyst so produced had a brown colour. The polymerization activity was 151 g/g TiCl_3 /h/98 kPa and the stereospecificity was 16.0%.

F. (Cf. Example 3 of Netherlands Patent

- 5 Application 7701019). A solution of 250 mmol. aluminium diethyl chloride, 170 mmol. di-isoamyl ether and 180 ml heptane was added dropwise at 35°C during 4 hours to a solution of 2000 ml TiCl_4 , 440 mmol. di-isoamyl ether and 120 ml
- 10 heptane. Thereafter stirring was continued at 35°C for 1 hour. Then the suspension was heated at 65°C for 2 hours, the liquid medium was removed by decantation and the catalyst was washed 5 times with iso-octane. The catalyst so
- 15 obtained had a purple colour and an irregular morphology, particle size was from 20 to 50 μm and a substantial portion of the particles had an irregular shape. The polymerization activity of this catalyst was 153 g/g TiCl_3 /h/98 kPa and the
- 20 stereospecificity was 11.0%. ** by 100%*

Example 9

The catalyst prepared in accordance with Example 8 was tested in polymerization of propylene in accordance with the liquid bulk

- 25 method.
- 3.5 l of liquid propylene monomer were introduced into a 5 l stirred autoclave at 60°C. Then 1.5 mmol. of diethyl aluminium chloride was added, followed by the introduction of 0.5 mmol.
- 30 TiCl_3 suspended in 10 ml. iso-octane. Another portion of 1.5 mmol. of diethyl monochloride was finally introduced thus giving an Al:Ti molar ratio of 6:1. H_2 was constantly supplied to the reactor to give a 2.0% vol. H_2 —concentration in the gas
- 35 phase in the reactor. No further propylene was added and the polymerization was continued for 4 hours at 60°C. Then the polymerization was stopped by releasing the pressure. This caused the remaining monomer to evaporate completely,
- 40 together with the small amount of iso-octane. The dry polymer powder was weighed and analyzed to determine particle size distribution, bulk density and xylene solubles content. Likewise, a small sample of the polymer suspension was taken at a
- 45 polymerization time of 2.5 hours in order to determine the polymer yield at that moment. Polymer yields are expressed as g polymer per g TiCl_3 and as g gram polymer per g TiCl_3 per hour.
- 50 Yield at 2.5 hrs: 7000 g/g TiCl_3 ; 2800 g/g TiCl_3 /h
Yield at 4 hrs: 9810 g/g TiCl_3 ; 2453 g/g TiCl_3 /h
Stereospecificity at 4 hrs: 5.7%
Polymer bulk density: 0.40 g/ml.
Particle size distribution: narrow, with regular, round polymer particles, exhibiting excellent
- 55 flow characteristics.

Comparative Example G

The catalyst prepared in accordance with Example F was subjected to the same polymerization method as described in Example 9.

- 60 Yield at 2.5 hrs: 7200 g/g TiCl_3 ; 2880 g/g TiCl_3 /h
Yield at 4 hrs: 9690 g/g TiCl_3 ; 2425 g/g TiCl_3 /h
Stereospecificity at 4 hrs: 8.2%
Polymer bulk density: 0.33 g/ml.

Particle size distribution: broad, with relatively high proportion of coarse particles.

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Example 10

Example 9 was repeated now using a H_2 —concentration of 1.4% vol. The following results were obtained:

- 70 Yield at 4 hrs: 7400 g/g TiCl_3 ; 1850 g/g TiCl_3 /h
Stereospecificity at 4 hrs: 7.2%
Polymer bulk density: 0.41 g/ml
Particle size distribution: narrow, with regular, round polymer particles, exhibiting excellent
- 75 flow characteristics.

Example 11

0.25 mmol. p-methoxy-ethyl benzoate was reacted with 3 mmol. diethyl aluminium chloride at 25°C during 10 minutes. Then the reaction

80 product, together with a suspension in 10 ml iso-octane of 0.5 mmol. TiCl_3 obtained in accordance with Example 8, was introduced into the polymerization reaction system described in Example 9. Polymerization was effected as

85 described in Example 9, apart from using a H_2 —concentration of 1.4% vol. The following results were obtained.

- Yield at 4 hrs: 6570 g/g TiCl_3 ; 1642 g/g TiCl_3 /h
Stereospecificity at 4 hrs: 4.3%
90 Polymer bulk density: 0.43 g/ml.
Particle size distribution: narrow, with regular, round polymer particles, exhibiting excellent flow characteristics.

Claims

- 95 1. A process for the preparation of an olefin polymerization catalyst comprising reducing TiCl_4 with an organo aluminium compound in the presence of a dialkylether, characterized in that TiCl_4 is reduced with a trihydrocarbyl aluminium compound in a molar ratio of Ti:Al of at least 2.7:1 in the presence of di-isoamylether and a hydrocarbon solvent by gradually combining the reactants at a temperature of from 65 to 90°C during a period of from 1.2 to 5 hours to produce
- 100 a precipitate of brown TiCl_3 , whereupon this precipitate is activated by heating at a temperature of from 80 to 110°C during a period of at least 30 minutes.
2. A process as claimed in claim 1, in which the
- 110 Ti:Al molar ratio is from 4:1 to 6.5:1.
3. A process as claimed in claim 1 or 2, in which tri-hydrocarbyl aluminium compound is a trialkyl aluminium compound in which each of the alkyl groups have from 2 to 8 carbon atoms.
- 115 4. A process as claimed in any one of claims 1 to 3 in which the reduction is effected by combining TiCl_4 , which has been premixed with di-isoamylether in a molar ratio of Ti:ether of from 1:1 to 2.4:1, with a trihydrocarbyl aluminium compound which has been premixed with di-isoamyl-ether in a molar ratio of Al: ether of from 1.4:1 to 0.6:1.
- 120 5. A process as claimed in any one of claims 1 to 4, in which the reactants participating in the reduction reaction are gradually combined during a period of from 1.5 to 3 hours.
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